HILTS

Composition & Properties
Of Portland Cement

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A STUDY OF THE COMPOSITION AND PROPERTIES OF PORTLAND CEMENT

...BY...

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Roy. W Hilts

ENTITLED *A Study of the Composition and Properties of Portland Cement.*

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OF *Bachelor of Arts.*

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Introduction.

Portland cement consists essentially of a mixture of certain anhydrous silicates and aluminates of calcium, possessing hydraulic properties, that is to say, when mixed with water, the mass combines chemically with it, and hardens. This hardening or setting takes place while the cement is still wet and may, indeed, even proceed under water. As distinguished from ordinary mortars, the setting and hardening of cement is not dependent upon the presence of carbon dioxid, and moreover the set cement is very insoluble in water, thus fitting it for use in positions where ordinary lime mortar would not be permissible.

The uses of Portland cement have been very widely extended during the last few years, and now engineers employ it in dams, walls, reservoir linings, bridge abutments, piers, pavements, sidewalks, and in a thousand other positions where resistance to water and high compressive and tensile strength make it a very desirable material, and bar the use of ordinary mortars. Since its range of employment is broadening at such a rapid rate, the consumption of Portland cement in this country has become very great, and hitherto a very large proportion of this amount has been imported from abroad. However, cement factories have now sprung up in various parts of the country, where, with the rotary furnace and modern methods, a product of very good quality is turned out to meet for the most part the great and rapidly growing demand for this

material.[#]

Portland cement is a development from Roman, or natural cement. This was first made in England by burning nodules of argillaceous limestone found along the Thames. Many deposits have since been found in other places, which furnish a natural cement. Such rocks are broken up and burned, but not to the sintering point, and then finely pulverized. They set quickly but have not the strength of Portland cement. It is noteworthy that the natural cements almost always have a magnesia content that would render a Portland cement useless.[26] At first much trouble was experienced with these natural cements, in that the results were variable and unreliable because of variations in composition of different parts of some of the deposits furnishing the raw material. Hence, after it was discovered that natural cements could be improved by the judicious use of limestone or clay, it was a natural development to make a cement by the proper combination of these ingredients alone. This product is true Portland cement, and its history dates from 1824. The raw materials for Portland cement are a pure limestone and a fine clay, magnesia in either to any considerable amount to be avoided. The

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[#] In this connection may be given a few data as to the extent and growth of this industry in the United States:[23]

Production

Year	Natural	Portland	Imports	Exports	Consumption
1890	2,161,000	4,989,000	2,325,000	70,000	13,734,000
1902	9,897,000	17,083,000	2,659,000	432,100	29,408,000

(In barrels of 300 lbs.)
The production has increased, on the average, 30 to 40 per cent per year for about eight years, so that three times as much cement was produced in 1902 as in 1894. In the same period the factories have increased three fold in number and some of the larger ones eight fold in capacity. (C. W. McKee in Min. Ind. 1902).
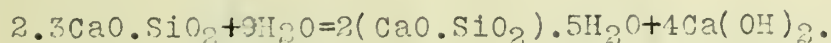
materials are very finely ground up, mixed, and then, either pressed into briquettes, or as a slush or "slurry", passed through a furnace, in which the temperature is sufficiently high to produce sintering. The "clinker" is then finely pulverized and aged, preparatory to use.

From a rule of thumb method, the manufacture of cement has come to be a scientific process, in which the various processes are under close chemical control, and the compounding of the materials is so nicely calculated that the composition, character and uniformity of the product is assured, granted that the mechanical side of the manufacture has been properly superintended. It must not be understood that theory at first set the limits for the various constituents of cement, which are, by the way, comparatively narrow. These were worked out arbitrarily from experience, in the first place, and it is only within a little less than twenty years that theories have been offered that profess to justify and fix more exactly the proportions of the components upon a scientific, chemical basis.

Research and Theories.

It is rather remarkable that the constitution of an important synthetic material such as cement, should be so little understood, but such is the fact, and we are not yet in a position to state conclusively the exact state of combination in a cement and the reactions involved in its setting. However, we now have theories that seem tenable and that are quite well substantiated by the facts. A Frenchman, Le Chatelier (1887), has been the pioneer in this field. The effort has long been made to find some method for

estimating uncombined lime in a cement. A good article should contain no free lime since this causes cracking and checking after it has set. Formerly it was thought that free lime could be determined by extraction of the pulverized cement with water. Le Chatelier, observing that lime so extracted was accompanied by small amounts of silica or alumina, declared that it was "combined" lime and not free as previously supposed.[1] He investigated the problem further and examined sections of the clinker and of the set cement under the polarizing microscope, and observed in the latter hydrated mono-calcium silicate and calcium hydrate, besides other definite crystalline compounds in both materials. Led by this, he made synthetically various silicates and aluminates of calcium, and investigated their hydraulic and optical properties. He thus made $CaO.SiO_2$ and $2CaO.SiO_2$, neither of which had setting properties, but was unable to get any well defined compound of higher calcium content. He found that the aluminates possed rapid setting qualities, and decided that the tri-calcium aluminate($3CaO.Al_2O_3$) is present in cement.[2] Summarized, his theory is this: The active constituents of burned cement are tri-calcium silicate ($3CaO.SiO_2$) and $3CaO.Al_2O_3$, besides some lower calcium silicates. Magnesia replaces lime, and iron replaces alumina in the compounds. The true hardening of a cement - and this requires months for completion - is due to the reaction

$$2.3CaO.SiO_2+9H_2O=2(CaO.SiO_2).5H_2O+4Ca(OH)_2.$$

The setting is largely due to the reaction

$$3CaO.Al_2O_3 + Ca(OH)_2 + 11H_2O=4CaO.Al_2O_3.12H_2O.[26]$$
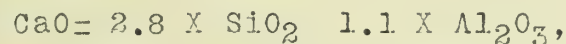
This latter statement, that the aluminates are concerned in the set-

ting is borne out by the fact that cements highest in alumina set with the greatest speed. From these theories Le Chatelier calculated the ratio of the basic to the acidic components of cement, the so-called "hydraulic index", and tested the truth of his conclusions by compounding and burning cements according to those formulae. They possesed good setting qualities. Le Chatelier's hydraulic index is defined by the following ratios:

$$\frac{CaO + MgO}{SiO_2 + Al_2O_3} \lesssim 3, \text{ and } \frac{CaO + MgO}{SiO_2 - Al_2O_3 - Fe_2O_3} \gtrsim 3.[26]$$

S. B. and W. B. Newberry repeated some of Le Chatelier's experiments (1897) and were more fortunate than Le Chatelier in obtaining, with a better furnace, what appeared to be a well defined tri-calcium silicate, which possesed remarkably good hydraulic properties.[3] They found that a silicate of greater basicity than this would not set. Thus far, their work corroborated Le Chatelier's theory, but with the aluminates, they decided that $2CaO.Al_2O_3$ was the most basic one permissible. They made and tested cements proportioned according to their own and Le Chatelier's formulas. With cements low in alumina, there was no appreciable difference, as might be expected. With cements high in alumina, however, Le Chatelier's formula gave a product that checked and cracked in setting, as if from free lime, while their own formula gave a sound set. This seems very fair evidence that Le Chatelier made his aluminate too basic. The Newberrys decided that magnesia does not replace lime, but is inert. It has been shown that freshly calcined MgO takes up water slowly, with expansion, and hence this seems to explain the fact that cements too high in magnesia are liable to crack with age.[4] The slowly hydrating magnesia, enclosed within the hardened surrounding material would shatter the mass by its slow expansion. The limit is set for MgO

at from 2 to 5 per cent.[26] Newberry and Smith have done later work
(1902) which confirms the synthesis of tri-calcium silicate.[6] By
calcining very finely powdered $CaCO_3$ and SiO_2, the tri-basic com-
pound is formed, having a specific gravity of 3.055 and free from
uncombined CaO or SiO_2. It sets slowly and hardens well. If the
above ingredients are heated for two hours at a red heat, basic com-
pounds are produced, but free SiO_2 is left, unless there is more
than 2 1/2 molecules of CaO. However, at a white heat, the various
mono-,di-, and tri-calcium silicates are completely combined. The
conclusions of the Newberrys are summed up in their formula for
Portland cement, which is

$$CaO = 2.8 \times SiO_2 \quad 1.1 \times Al_2O_3,$$

where the factors 2.8 and 1.1 are the ratios of CaO to SiO_2 and
Al_2O_3 respectively, in $3CaO.SiO_2$ and $2CaO.Al_2O_3$.[26]

The comparatively small amount of the alkalis always present
in cement, was at one time thought essential to act as a flux in
the burning of the material, but experiment has shown that a cement
can be burned without them and they are accordingly not active. A-
mong other accessory constituents is carbon dioxide,for this is nev-
er completely expelled in the burning,and moreover is taken up in
the process of aging, the purpose of which is to permit atmospheric
CO_2 to combine with any free CaO present after burning and grinding.
Also, some sulphur is present both as sulphide and sulphate, com-
ing largely from the sulphur in the fuel, or from gypsum, which is
sometimes added to retard the setting. Although a little $CaSO_4$ may
thus be beneficial, 4 to 5 per cent is undoubtedly harmful, the
limit set by engineering specifications being generally 2 per cent
of SO_3.[26]

The theory of the Newberrys on the constitution of cement is the one that finds the most general acceptance at present. Richards (1903) has recapitulated the theory in a somewhat later form.[5] It is substantially as follows: Portland cement consists essentially of a solid solution of $3CaO.SiO_2$ and $2CaO.Al_2O_3$, containing 85% of the former and 15% of the latter. In commercial cement, an iron-lime compound replaces more or less of the aluminate. The MgO, sulphates and alkalis are non-essential and should not be present in amount sufficient to interfere with the formation of the solid solution. For good cement the silicate must be a tri-basic form.
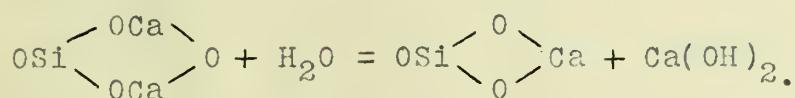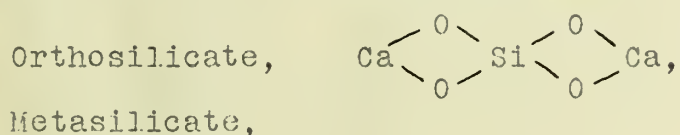
That the constitution of cement and the chemistry of its reactions are not conclusively settled to the satisfaction of all investigators, is proven by the large number of theories that have appeared in the last few years. A short review of some of these researches and theories proves suggestive, at least.

N. Ljamin (1898) has worked out some methods for the estimation of $Ca(OH)_2$ in set cement.[11] The first is a specific gravity method depending upon the use of a heavy solution of benzene and methylene iodide. The second depends upon the fact that $Ca(OH)_2$ loses water at a temperature far above that at which the other hydrated compounds are dehydrated. Ljamin claims that the methods give concordant results. Using the latter, he made determinations of the amount of $Ca(OH)_2$ in a set cement at various periods, and found an increase continuing for some months, when something over 33% was present.[17] Basing it upon this fact, Ljamin made a statement, that the hexagonal crystals of $Ca(OH)_2$ (visible under the microscope) play a large part with the increase of strength of the cement during

its hardening period.

Wegener (1900), in commenting upon the specific gravity method of Ljamin for the determination of $Ca(OH)_2$ in hardened cement, condemns it as impracticable and gives it as his opinion that the absorption of CO_2 by the CaO in calcined cement promises a more accurate means of estimation.[14] He found that CO_2, although completely expelled from the mass at 1000°C. was greedily absorbed at 800°. From a lack of data the writer was unable to draw final conclusions as to the accuracy of this method.

K. Zulkowski (1901) says that hexavalent silicic acid is unknown, thus denying the possiblity of a tri-calcium silicate. He claims that the so-called tri-silicate consists of a mixture of di-calcium orthosilicate (not hydraulic) and di-calcium metasilicate (active) and free lime.[12] The formulas of these compounds, and the setting of the latter are represented thus:

$$\text{Orthosilicate,} \qquad Ca \underset{O}{\overset{O}{\diagdown\diagup}} Si \underset{O}{\overset{O}{\diagdown\diagup}} Ca,$$

Metasilicate,

$$OSi \underset{OCa}{\overset{OCa}{\diagup\diagdown}} O + H_2O = OSi \underset{O}{\overset{O}{\diagup\diagdown}} Ca + Ca(OH)_2.$$

Ludwig (1901) arrives at the conclusion that in burning cement, there is first formed a calcium-aluminum-silicate or a calcium-iron-silicate.[7] He makes the statement that a pure tri-calcium silicate can not be made, since a flux must be present. He considers the alumina and iron to play this part in practice, and that any excess of CaO present over the amount requisite for the silicate, is combined with the alumina, and that this latter compound has much to do with the speed of setting. Free lime is not present in good
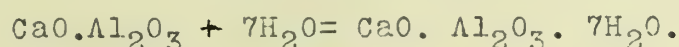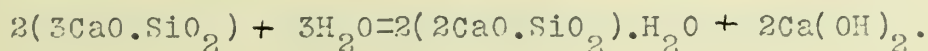
cements, according to Ludwig, and in this he agrees with the gen-
erally accepted view.

A. Meyer (1901) gives a somewhat more elaborated theory on
the composition and setting of cements.[8] He agrees that $3CaO.SiO_2$
is the most important constituent and says that this is associated
with a matrix of the material that has served for its formation.
There is thus a mixture of tri- and di-calcium silicates, a calcium-
aluminum silicate, and calcium aluminate, especially in weakly
burned cements. For the setting of the principal ingredient he
gives

$$3CaO.SiO_2 + 2H_2O = CaO.SiO_2(anhydrous) + 2Ca(OH)_2$$

It is to be noted that he disagrees with Le Chatelier, who claimed
to have detected crystals of _hydrated_ metasilicate in set cement
and assigned to them an important role in the process of hardening.

O. Rebuffat (1899) gives the active constituents of cement,
after setting, as $Ca(OH)_2$, hydrated calcium ortho-silicate $2(SiO_2.$
$2CaO).H_2O$, and various hydrated calcium aluminates, either mono-,
di- or tri-calcium compounds, but usually the first two, besides
certain secondary constituents.[9] With many more siliceous cements, a
cetain amount of metasilicate ($CaO.SiO_2$) must be assumed, which _does_
not form a hydrate but combines with the aluminates to calcium-al-
uminium silicates. Rebuffat claims that the degree of hydration of
the aluminates is in doubt since it is different in pure water and
in lime-water. The setting of the cement he ascribes to the hy-
dration of the silicate and of the aluminates, thus:

$$2(3CaO.SiO_2) + 3H_2O = 2(2CaO.SiO_2).H_2O + 2Ca(OH)_2.$$
$$CaO.Al_2O_3 + 7H_2O = CaO. Al_2O_3. 7H_2O.$$

A word may be said here concerning the phenomena of setting

and hardening of so-called hydraulic compounds, or mixtures, as ce-
ment. The compressive and tensile strength displayed by a mass
of such material, after moistening with water, must be explained
by the formation and the intricate interlacing of the mass of crys-
tals of the various hydrates which the dry material is capable of
forming. Throughout this network of "active" compounds runs a mat-
rix of secondary and inert material, and the less this is in amount,
the higher will be the strength of the mass.

E. Jex (1900) differs from the commonly accepted view, in con-
sidering that cement clinker contains free lime and alumina, the
essential compound being calcium orthosilicate.[10] When treated with
water the molecule of CaO associated with the metasilicate breaks
off to form the stable $Ca(OH)_2$. Along with this reaction goes the
hydration of the lime and alumina contained free in the clinker.

W. Michäelis has performed some rather unique experiments which
he claims shed some light upon the chemistry of the setting of cem-
ent.[16] He observed the increase of volume undergone by cement when
agitated with an excess of water, and found it to be considerable.
He then found by experiment that SiO_2, even pulverized rock-crys-
tal, and also $Fe(OH)_3$ and $Al(OH)_3$, when kept in contact with lime-
water, swell up and give quite well defined hydrated compounds, as
follows:

$2SiO_2.3CaO + xH_2O$, decomposed by water with relative difficulty,

$2Fe_2O_3.4CaO + yH_2O$, easily decomposed by water,

$2Al_2O_3.5CaO + zH_2O$, decomposed by water with relative ease.

The above, Michäelis claims, is the first instance of the success-
ful preparation, by a cold process, of a crystallized, hydrated
calcium silicate. He applys the above facts to an explanation of

the constitution of set cement.

Hart (1899) attempts to estimate free lime in burned cement by the use of a solution of iodine in absolute alcohol, and arrives at the conclusion that the clinker contains 30% of it.[19] Wormser and Spanjer tried to accomplish the same end by employing a dilute solution of $AlCl_3$ in the same solvent.[18] They claimed that the silicates are not attacked by this extractive solution, and their results led them to believe that 25% of lime is present in the free state. Considering the comparative instability of the highly basic compounds believed to be present in cement, such conclusions must be regarded with suspicion.

S. Wormser (1900) has done some work relative to the behavior of cement to ammonium salts, in the dry state.[20] He rubbed together dry cement and ammonium chloride and declared that the odor of ammonia then perceptible (easily verified) shows the presence of free lime. The mixture was then treated to the volatilization of the ammonium salt. In this process a part of the iron is expelled as chloride and the remainder is left scattered throughout the light friable mass in specks of red oxide. The $CaCl_2$ is next extracted with absolute alcohol, and estimated. The residue is ignited with the filter paper and boiled with HCl. Variable amounts of impure SiO_2 are here left insoluble and filtered out. This is fused up, recovered in the usual manner and the filtrate added to the main portion, for the analysis of the remainder of the cement. A remarkable fact was here observed: Although the residue from the alcohol extraction displayed almost no hydraulic properties whatever, if the amount of CaO extracted was again added and intimately mixed, the mixture showed good setting qualities. About 48% of CaO

was found in the alcohol extract, present in the cement - according to Wormser - partly as free lime and partly in easily decomposable compounds. His conclusions were as follows:-

1. Free CaO is changed into the chloride.

2. Monocalcium silicates or aluminates are not attacked, or only slightly.

3. Polycalcium compounds are broken down to a small stable residue. According to Wormser the cement contains about

$$CaSiO_3 \quad - - 14\%$$
$$Ca_2SiO_4 \quad - - 43\%$$
$$2CaO.Al_2O_3 - - 23\%$$
$$CaO \quad - - 20\%$$

From similar experiments with ammonium carbonate, he came to the following conclusions:-

1. Free CaO, if not present to exceed 40 % is entirely transposed to $CaCO_3$.

2. Monocalcium silicates and aluminates are not attacked.

3. From the polycalcium silicates, the CaO in excess of the metasilicate splits off, and at the same time a small part of the silicate is completely decomposed, this proportion increasing with the basicity of the compound.

4. Di-calcium aluminate is not broken down completely, but the CaO in excess of the mono-calcium compound, is changed into $CaCO_3$.

Although Wormser's work is interesting and doubtless suggestive of methods for differentiating the various compounds in cement, he is not sufficiently circumspect in his conclusions. Michäelis, commenting upon Wormer's results, says that the evolution of Ammonia

observed upon mixing dry cement and NH_4Cl, is not necessarily due
to the presence of free lime.[13] He noticed a similar result with
fused slag, powdered lime glass and even Cararra marble. This latter
statement is verified in a way, by Cantoni and Goguelia (1904) who
found that the alkaline-earth carbonates can be transposed in quan-
tity, by a solution of NH_4Cl.[28] Regarding critically the methods
employed by Wormser, Spanjer, Hart and others who claim to have
demonstrated the presence of free lime in good cements, and consid-
ering the instability of these highly basic compounds, we must agree
with Ludwig, who declares that such methods merely show that the
reagents employed are capable of splitting CaO out of such combina-
tions.[7] If appreciable quantities of free lime were present in a
sound cement, this should be shown by the absorption of CO_2 after
ignition. The investigations of R. & W. Fresenius, in connection
with cement adulteration, showed almost _no_ such absorption.

With reference to the practically important problem of esti-
mating free lime in cement, the work of Keiser and Forder (1904)
deserves mention.[22] Their method is based upon observing the amount
of water taken up by the material, after intense ignition, on expos-
ure to moist air. They tested the method by determining the amount
of water thus taken up by a cement, before and after the addition
of given quantities of CaO. The data checked well with theory, but
the fact that under the given conditions even a sound cement takes
up a certain amount of water, attributed to the hydration of easily
reactive aluminates, makes the method very approximate, to say the
least.

In connection with the chemistry of Portland cement, a word

should be said regarding a very peculiar phenomenon that has been observed by a number of investigators. Schütt, Meyer, Dyckerhoff and Heinztzel (1900) have reported cases in which a cement, during storage, has changed from slow setting to very rapid setting.[21] In some cases specimens that set originally in from 2 1/2 to 4 hours, set in from 15 to 20 minutes. Accompanying such changes there has been observed a great increase in the fineness of pulverization of the cements and this is doubtless the immediate cause of the greater speed of setting. Such changes and "self-pulverization" have been induced artifically in the laboratory by exposing the cement to the air, spread out in thin layers. This is a remarkable and unexplained fact.

Summing up our present knowledge of the chemistry of cement, we must admit that it is quite indefinite and that the differences of opinion are very numerous. As yet there is no accurate method for estimating free lime in the burned material, which would be a determination of great value in predicting the conduct of a given cement, with age, i.e., its soundness. It is now possible to detect adulterations with tolerable certainty, if present in any quantity, but for determining the physical behavior of a cement, its speed of setting, strength, liability to crack and check, etc., the engineer must rely wholly upon the various physical tests, which are not entirely satisfactory. Some undesirable qualities, as shattering or crumbling, develop only with age. A mere chemical analysis shows very little. The basic and acidic constituents may be in the proper ratio and yet the cement may be very poor, owing to various physical conditions. The raw materials may not have been ground

fine enough to secure very intimate mixture and correspondingly
complete combination, or the temperature of burning may have been
too low. Accordingly, it is very desirable to find some methods of
analysis, that will give the amount of the constituents, present in
the form of those active compounds that give Portland cement its
strength and setting qualities. This would be a very acceptable
supplement to the physical tests, at least, and might in part re-
place some of them. The studies here begun of some of the reactions
of the cement compounds, were undertaken in the hope that they
might point the way to some such methods of analysis, or throw more
light upon the constitution of this interesting material.

Experimental Results.

Cement Analysis.

The cement selected for use in these experiments was of the Alsen brand, a German Portland. For use in interpreting the results obtained in the various decompositions, a fairly complete analysis was made of the sample. The method was that of solution in HCl as per Meade, pp. 30-32.[26] Alumina and iron were reprecipitated and the lime was weighed as CaO, obtained by ignition over the blast lamp. The sample was dried for 1 hour at 110° in the air-bath.

Table 1. Analysis of Alsen Cement, dried at 110°.

	A	B	Mean
SiO_2	20.43%	20.33%	20.38%
$Al_2O_3 + Fe_2O_3$	10.63%	10.61%	10.62%
CaO	63.69%	63.80%	63.74%
MgO	2.26%	2.25%	2.25%
Loss on ignition	2.11%	2.24%	2.17%

Moisture in Air-dry Sample, 0.27% expelled at 110°, 0.40% at 165°.

The decompositions studied may be considered, in general, under two heads, the reaction with an aqueous solution of ammonium chloride, and the result of treatment with an excess of water. The latter will be considered first.

Decomposition by Water.

By treatment with water in excess we should expect to obtain

the CaO of easily decomposed compounds, especially the aluminates, which react easily with water and are thus the active agents in the setting, as has been noted, and also more or less CaO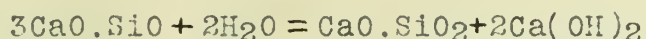 split out of the highly basic silicates, corresponding to the reactions of the hardening process. Alumina or silica, if any is set free, will be left in the insoluble residue. Qualitative experiment showed that agitation and standing with water in the cold, extracted a very considerable quantity of CaO, accompanied by practically no alumina or silica. The following experiments were accordingly made: The idea was to decompose the cement with water in the cold, to filter off the water extract so obtained and finally to wash the residue with a solution of cane-sugar, in which CaO is much more soluble than in pure water. Thus the freed lime would be filtered off and extracted with a neutral solvent incapable of attacking the still undecomposed portions of the cement. Apparatus was arranged by which the processes of decantation and filtration could be performed in a closed flask, by means of a filtering tube and cotton filter, without exposing the alkaline extract to atmospheric CO_2, thus preventing precipitation of $CaCO_3$. Two pulverized and dried (110°) samples of about a gram each were weighed out into 200 c.c. Erlenmeyer flasks provided with rubber stoppers, 100 c.c. recently boiled water was added and the flasks violently shaken for 15 minutes. Decomposition very rapidly gave a mass of flocculent material—alumina— which subsided quickly upon standing and left a clear supernatant liquid. After two or three weeks some small, white, well defined crystals were observed in the mass. The flasks were allowed to stand for 30 days with almost daily shaking. The

water extract was then decanted and filtered off by the filtering
arrangement and two portions of about 125 c.c. of a 5% sugar solu-
tion were run into the flask, the flocculent residue agitated there-
with, the solution decanted through the filtering tube and the mass
sucked dry. It was calculated that the three decantations were
sufficient to remove the CaO almost completely. One extract was
lost by the collapse of a flask under suction, and accordingly the
crystals above mentioned were removed from the residue and examined
under a glass. They were opaque, white, hexagonal prisms. When
placed upon moistened red litmus paper, the paper was perceptibly
blued under them. When treated with dilute HCl under the micro-
scope, the crystals were observed to dissolve slowly without ef-
fervescence. Their appearance and form corresponds to the descrip-
tion of crystallized Ca (OH)$_2$ observed by Michaelis under similar
conditions.[16] The combined water and sugar solutions were acidified
and CaO determined in duplicate upon aliquots of 1/20. All of the
CaO determinations in these experiments were made by permanganate
titration, unless otherwise specified. The insoluble residue was
dissolved in hot HCl, the insoluble matter filtered out and weigh-
ed, and SiO$_2$ determined in the filtrate. The above was similarly
repeated with two more samples, except that the decomposition con-
tinued only for 46 and 50 hours respectively. Results as follows:

Table 2. Decomposition by Water.

Time	30 days.	46 hrs.	50 hrs.
CaO in extract	23.58%	12.50%	11.81%
SiO$_2$ in residue	20.94%	------	------
Insoluble in HCl	0.67%	------	------

"Insoluble in HCl" merely represents the insoluble matter in the original cement. We see that CaO to the extent of 11 or 12 per cent. of the sample goes into solution with comparative ease but that further decomposition proceeds slowly, and there is no assurance that the maximum amount was extracted in 30 days. It is interesting to note that the "CaO of decomposition" in the shorter periods approximates 11.7%, the amount of CaO required by theory to form $2CaOAl_2O_3$ with the 10.62% of Al_2O_3 ($+Fe_2O_3$) present in the cement. The reaction which proceeds slowly probably corresponds to something like

$$3CaO.SiO + 2H_2O = CaO.SiO_2 + 2Ca(OH)_2$$

which has been given to express the setting of tri-calcium silicate.[26] This seems confirmed by the fact that none of the silicates seemed to be completely broken down, since practically no free SiO_2 was found, and also by the fact that the increase of $Ca(OH)_2$ in a hardening cement, believed to be due to the above reaction, is also very slow. Apparently the CaO extracted by water, in excess of that from the aluminates, is split out of poly-basic compounds which are not completely broken down.

Boiling with Sugar Solution.

Since reactions as inconveniently slow as the above did not promise much, it was determined to see whether the same decomposition could not be more quickly produced by boiling with a sugar solution, which, while neutral, would increase the solvent power of the solution for CaO[29] and should thus accelerate the reaction. For this, 200 c.c. of a 5% sugar solution was heated to boiling under

a reflux condenser, and 1.0 gram of pulverized and dried cement brushed in, the condenser replaced and the boiling continued for from 1 to 3 hours, with occasional shaking. The residue was flocculent in character and settled rapidly. Filtered hot and determined in CaO in each filtrate in duplicate on aliquots of 1/5. Solutions from the first and last samples gave a very slight precipitate upon making ammoniacal preparatory to calcium precipitations, but this was disregarded.

Table 3. CaO in Sugar Solution Extract.

Sample	Time	CaO (Mean)
A	1 hour	9.08 %
B	1 "	7.88 %
C	3 "	9.84 %

Since the results appeared so irregular and moreover, as the reaction did not seem to be greatly hastened, these experiments were abandoned.

Extraction of Free SiO_2 from Residues.

Before passing on to the NH_4Cl decompositions, we must give some attention to a troublesome analytical problem that appears in that connection. This is the separation of free, from combined silica. In these decompositions a certain amount of SiO_2 is precipitated in granular form from decomposed silicates, and it is very desirable to separate this from the undecomposed silicates and aluminates present, as an aid to the interpretation of the results. Practically the only method of accomplishing this is by extraction with Na_2CO_3 solution (see Cairns, p. 87, and Fresenius Quant. Anal.

5th ed. Sec. 236). Others have recommended caustic alkalis. At
best, it is not a highly accurate separation and it is particularly
unsatisfactory when dealing with easily decomposed compounds as in
the present case, but it is the best available. A number of re-
sidues obtained by treating with HCl the insoluble matter left after
boiling cement with NH_4Cl solution, were digested with hot 2% KOH.
Qualitative and roughly quantitative experiments showed that even
this dilute alkali was a fairly good solvent for such SiO_2, even af-
ter ignition, and that it dissolved part, but not all of the alumina
present in such residues. Freshly precipitated $Al(OH)_3$ was dissolv-
ed with ease, but after ignition, the Al_2O_3 went into solution with
difficulty and imperfectly. It was thought desirable to find the
effect of these solvents for SiO_2, upon the fresh cement, as this
would help to show whether the cement compounds were decomposed by
such treatment, and would throw light upon the reliability of such
silica extractions, since qualitative experiment showed that a lit-
tle SiO_2 was thus extracted from the cement. Samples of 1. g. of
oven-dry and pulverized cement, were boiled for 15 minutes with 50
c.c. of a 2% KOH solution, in covered casseroles. The solution was
decanted through a filter and the residue boiled up again with 25
c.c. of the same solution, which was then decanted and the residue
filtered and washed. The combined filtrates were acidified with
HCl and SiO_2 determined in them, this being corrected by expulsion
with HF. The extractions yielded respectively 0.48% and 0.50% of
SiO_2. More than 1% of Al_2O_3 was extracted along with the silica.
The result is not bad, considering that platinum dishes were not
used and that the cement does contain a little uncombined silicious

material. When the residue from KOH digestion is treated with acid, there is some little effervescence. This probably results from the precipitation of CaO from easily decomposed aluminates by the CO_2 in the alkali, but it may indicate some decomposition or splitting up of the silicates and is not a good sign for the reliability of the method.

A strong solution of Na_2CO_3 (20%) was used for extraction of SiO_2 in some of the experiments as it was feared that dilute KOH was not active enough. The experiment with dried cement was repeated with this solution. One gram samples were boiled up with 20 c.c. of Na_2CO_3 solution, for 15 minutes, in covered casseroles, and after decantation the operation repeated with 10 c.c. of the same solution. These filtrates were acidified and SiO_2 determined as usual, but the silica was not treated with HF, as a number of such experiments had shown that SiO_2 thus extracted and determined was practically pure (0.2-0.4 mg. residue) since the carbonate solution dissolves little alumina. The extracts gave 3.23% and 2.96% SiO_2, mean 3.10%. The residue effervesced vigorously when treated with acid. This shows that the carbonate disintegrates some of the silicates in cement in such a manner as to extract a certain amount of silica. In some of the later determinations, a 5% solution of Na_2CO_3 was adopted for the extraction of free SiO_2, following the recommendations of Lunge and Millberg.[27] The same experiment was tried with this. A sample of 1.0 gram of dry cement was brushed into 50 c.c. of the solution in a small covered casserole, and then heated and kept at a gentle boil for 15 minutes. The carbonate solution yielded 2.32% SiO_2, corrected by HF. It must be remembered that although

these results seem disappointing, the fact that these solvents de-
compose compounds in the cement proper, does not prove that they do
the same in the residue of compounds left by ammonium chloride.

Decomposition of Cement by NH_4Cl.

Decompositions of cement by ammonium salt solution will now be
described. It has long been known that cement contains compounds
which break down in an aqueous solution of NH_4Cl, lime going into
solution and ammonia escaping. Le Chatelier states that his syn-
thetic $CaO.SiO_2$ did not decompose with ammonium salts, although
$2CaO.SiO_2$ did so. He claimed that the crystals of $CaO.SiO_2.2\ 1/2$
H_2O, which he observed in set cement, decomposed instantly with am-
monium salts, with separation of gelatinous silica.[2] Wormser's work
with cement and NH_4Cl in the dry, might again be mentioned.[20] In the
present experiments it was found that water solutions of $(NH_4)_2\ SO_4$,
$(NH_4)_2CO_3$ and ammonium oxalate, reacted with cement even in the
cold, but more slowly than the chloride, and moreover there was the
disadvantage that a large portion of the CaO of the decomposed sili-
cates and aluminates was left in the residue as insoluble compounds
and thus could not be determined. For this reason and for conveni-
ence of manipulation, the chloride was chosen for experiment. It
was hoped that by a study of the proportions of the decomposition
products, ammonium chloride would afford some means of different-
iating the compounds in cement by means of their behavior towards it
and would thus give some information on the constitution of the mix-
ture or offer a means of estimating some of the compounds present.

In the first place, it is necessary to find whether the reac-

tions of the decomposition are quantitative, and if so, under what conditions. In general, the effect of boiling cement with NH_4Cl solution is this: Ammonia is evolved and calcium goes into solution as the chloride. The aluminates decompose entirely and flocculent alumina precipitates. Some of the silicates are broken down with separation of <u>granular</u> silica. If this residue, after filtering off the NH_4Cl solution, is treated with hot, dilute HCl, the remaining compounds go into solution, together with most of the alumina, and the separated SiO_2 is left, along with a little of the alumina. The separated SiO_2 has about the same appearance as that obtained by de-hydration in the course of an ordinary silica determination, filters well, and is very white after ignition. The silica thus obtained, although it contains some alumina and the other matter insoluble in HCl(0.6% by experiment) is a rough index of the extent to which the silicates have been decomposed. Accordingly samples of 1 gram of the cement were boiled with NH_4Cl solutions of different volume and concentration- from 1 to 5 grams NH_4Cl in 100 c.c. water- and the silica obtained as above was ignited and weighed. The duration of boiling was varied, some samples were evaporated to dryness and others were finally baked in the air-bath. Some of the solutions were kept strongly ammoniacal during boiling and some were heated in the autoclave. Results were extremely variable, running from 0.1186 g. to 0.2099 g. of SiO_2, the average being 0.17-0.18 g. Ammonium carbonate was tried with NH_4Cl, as for a time it seemed that this might give concordant results. Variations were so great that duplicates could hardly ever be obtained, so this method was given up and a more careful study of the proportions of the decomposition

products was made, in the hope that something more definite might be learned about the reaction.

A sample of cement was pulverized in the agate mortar, dried at 110° and two samples of 1 g. each weighed out. One and two grams of NH_4Cl were dissolved in 100 c.c. water, these were brought to a boil in a beaker, the sample brushed in, and boiling continued for 30-35 minutes. The solutions were then evaporated to dryness and the residues heated at 125° for some time. Took up in water, filtered and washed, obtaining thus the "NH_4Cl extract. It was determined to extract the SiO_2 from the residue by means of caustic alkali, for it was feared that when the mass was treated with HCl, a portion of the separated silica might go with solution. Accordingly the residue was digested with 50 c.c. of 2% KOH for 1/2 hour. It was filtered and washed, obtaining the "KOH extract". Lime was determined in duplicate in aliquot portions of the NH_4Cl extracts and tests for SiO_2 and Al_2O_3 were made in separate aliquots. The whole of the KOH extracts were used for analysis. Silica was corrected by HF.

Table 4. NH_4Cl Decomposition.

Sample	NH_4Cl Extract		KOH Extract	
	A	B	A	B
CaO	50.92 %	57.51 %	0.23%	0.19 %
MgO	0.00	0.00	trace	trace
SiO_2	0.00	0.00	5.39	7.07
$Al_2O_3 + Fe_2O_3$	Mean- 0.17		1.18	0.86

Sample A was decomposed with 1 g. NH_4Cl in 100 c.c. and B with 2 g. It is evident that the greater concentration of NH_4Cl produced the greater decomposition. It is interesting to note that, although

the cement contains 2.25% MgO, none was found in the NH_4Cl solution,
which contained practically nothing but $CaCl_2$. The CaO in the KOH
extract has no significance as regards the decomposition effected
by the NH_4Cl, but it must indicate a breaking down or partical dis-
integration of the compounds left by the NH_4Cl, and thus throws some
doubt upon the SiO_2 values. Considering the analysis of the cement,
we find that in B, the ratio of CaO to SiO_2 not extracted is

$$\frac{63.74-57.51}{20.38- 7.07} = 0.468 .$$

which is far below the ratio even in $CaO.SiO_2(0.927)$. This shows
that the dilute KOH must have failed to extract all of the SiO_2 set
free, since $CaO.SiO_2$ is the least basic compound that can be assum-
ed for the residue of undecomposed silicates. Sample A also gives
too low a ratio. Moreover, the preliminary experiments never gave
such low results for SiO_2 of decomposition.

Another and similar experiment was made, using strong Na_2CO_3
for extracting SiO_2 from the residue. Four portions of about 1 g.
each of the same dried cement were weighed out. Samples A and B
were boiled down to about 1/4 volume with a solution of 0.5 g. NH_4Cl
in 100 c.c. water and samples C and D with a solution of 1 g. in
100 c.c. They were evaporated to dryness, washed by decantation
with hot water and the filtrates made up to volume as NH_4Cl ex-
tracts. The residues, with incinerated filter paper, were twice ex-
tracted by boiling in casseroles for 15 minutes with 20 c.c. of a
20% Na_2CO_3 solution (20 g.Na_2CO_3 in 80 c.c. water). The united car-
bonate solutions gave the "Na_2CO_3 extracts ". In the case of the
NH_4Cl extracts, the CaO was determined gravimetrically in aliquots
of 2/5. Ammonia gave a very slight precipitate which was filtered

out before precipitating calcium, but not weighed.

Silica was corrected by HF.

Table 5.   NH₄Cl Decomposition.

Sample	NH₄Cl Extract		Na₂CO₃ Extract of residue		
	CaO	MgO	SiO₂	Al₂O₃+Fe₂O₃	CaO
A	26.58%	trace	6.90 %	0.68%	0.27%
B	27.39	"	7.40	0.54	0.33
C	46.61	little	10.46	0.76	0.29
D	45.51	" .	10.26	0.88	0.28

When the residue from Na₂CO₃ digestion was treated with acid
it effervesced vigorously. This shows some reaction between the
Na₂CO₃ and the compounds left by the NH₄Cl, and suggests that more
SiO₂ may have been extracted than that which was separated during
the NH₄Cl decomposition, which it was desired to estimate. The
Al₂O₃ and CaO in the Na₂CO₃ extract have no particular significance
here but merely represent their degree of solubility in this solu-
tion. Assuming that the aluminates are di-basic (Newberrys)[3] and
completely decomposed, they would give 11.7 % CaO from this source
and if we add to this the CaO corresponding to the SiO₂ extracted,
as 3CaO.SiO₂, this theory would require 4 to 5 per cent more CaO
than found in the case of A and B and 5 to 6 per cent less than
found in C and D. In the latter case we must apparently assume not
merely disintegration of some of the silicates, but the splitting
out of lime from others to form less basic compounds.

It was feared that the irregularities of the NH₄Cl decomposi-
tion at the boiling temperature might be due to the dissociation
which that salt undergoes, even on boiling its solution, into HCl
and NH₃ , thus giving free acid which would naturally vitiate the

results. Accordingly a sample of the cement was allowed to stand
42 hours with a 2 % NH₄Cl solution in the cold, with occasional ag-
itation. The aluminates seemed to be very completely decomposed
after a few minutes shaking. The residue was filtered and washed
cold. The filtrate contained 47.26 % of CaO. As the reaction ap-
peared to proceed with considerable speed, it was repeated thus:
Two samples of 1.0g. of oven-dry cement were brushed into 200 c. c.
Erlenmeyer flasks containing 100 c.c. of 5 % NH₄Cl solution (5grs.
in 95 c.c.). These were shaken for a time and let stand for differ-
ent periods with occasional agitation. They were filtered and
washed cold and CaO determined in duplicate upon aliquots of 1/5 of
the filtrates. These contained no SiO₂ or Al₂O₃. The residue from
sample A was digested for a few minutes with hot dilute HCl and the
insoluble SiO₂filtered off, weighed and corrected by HF. The resi-
due from sample B was extracted with 50 c.c. of 5 % Na₂CO₃ solution,
as recommended by Lunge and Millberg for SiO₂ extraction.[27] The res-
idue was washed into a casserole with the solution and it was then
kept at a gentle boil for 15 min. Silica was determined in this
carbonate extract. The residue still left was digested with hot
acid, as in sample A, and the silica so obtained was weighed and
corrected by HF (SiO₂ "left by HCl"). Results seemed so concordant
(see table 6) that the experiment was repeated with three more sam-
ples. The CaO values are the mean of duplicates agreeing in gener-
al within 0.1 % or less.

Table 6. NH_4Cl Decomposition in the Cold.

Sample	NH_4Cl in 100 cc. Sol.	Time	CaO in Filtrate	Silica from Residue		
				Na_2CO_3 Ex.	Left by HCl [a]	Total
A	5.0 g.	47 hrs.	47.79%	(Not extracted)	16.75%	16.75%
B	5.0 "	7 days.	47.76	12.75% [a]	3.89	16.64
C	5.0 "	24 hrs.	45.02	12.04	3.16	15.20
D	5.0 "	47 "	46.20	12.16	3.60	15.76
E	10.0 "	6½ "	47.77	12.46	3.54	16.00

(a) Corrected by HF

When dilute acid was poured on the residues from the Na_2CO_3 digestions, carbonates were always observed as in the previous cases. It is difficult to say what is the condition of the SiO_2 left by the HCl. Evidently it is not freed in the decomposition by NH_4Cl, or it would then be extracted by Na_2CO_3, but must exist in altered compounds which upon dissolving in HCl separate granular silica. Its quantity is fairly constant. The decomposition, in the case of A, B and E seems to have reached quite a definite limit and to be quantitative under these conditions. The CaO of decomposition is surprisingly concordant and the SiO_2 of the decomposition sufficiently so, considering the imperfections of the method of estimating it. Selecting the two most widely varying samples in the table, B and C, let it be assumed that 11.7% CaO comes from the alumina in the cement as $2CaO.Al_2O_3$, and that the free SiO_2 extracted by Na_2CO_3 comes from completely decomposed $3CaO.SiO_2$. Then theory would require 47. 2% CaO as against 47.76% found, and 45.2% CaO as against 45.02% found. This is very fair agreement of the theory with the facts observed, and goes to show that the CaO dissolved by the NH_4Cl solution comes

from the disintegrated aluminates and tri-calcium silicate. The silicates that are left by the NH_4Cl (or Na_2CO_3) are differentiated by the fact that a part of the silica is obtained in granular form and a part goes into solution on treatment with HCl. Hence two different silicates at least, must be in this residue. It is almost impossible to guess at their constitution, for the MgO in the cement, although considered inert as a hydraulic constituent, may be combined with a part of the remaining silica.

A study of the speed of decomposition of cement, by NH_4Cl in the cold, was next made. The method was the same. Each sample of 1.0 g. of oven-dry cement was shaken for 15 minutes with 100 c.c. of a 10% NH_4Cl solution and then agitated periodically (every half hour) for varying lengths of time. Filtered and washed cold. The last three decompositions, G-I, were not made upon the same dried sample as the first six, but upon a new one. The results are the mean of well concordant duplicate titrations.

Table 7. Speed of Decomposition with 10% NH_4Cl Solution.

Sample	A	B	C	D	E	F	G	H	I
Time in hours	1	2	3	4	5	6	7	8	9
CaO in filtrate	44.88 %	45.65	46.58	47.03	48.01	48.69	47.48	47.70	47.78

The reaction appears to have reached its limit in from 6 to 9 hours. The only reason that could be given for the higher CaO results in E and F, was that during the drying of the sample upon which these determinations were made the temperature accidentally rose for a time much higher than 110°. The last three results agree well with the maximum values in table 6.

An examination of the results in tables 6 and 7 led to the be-
lief that agitation might have much to do with the speed of decom-
position. Therefore three samples of 1.0 g. of the same oven-dry
cement as G-I of the previous experiment, were similarly decomposed,
except that the stoppered flasks were tied upon a revolving wheel
and the contents thus kept in gentle but continuous agitation. CaO
extracted was as follows:

Table 8. Influence of Agitation.

Sample	Time	NH_4Cl Sol.	CaO (Mean)
A	6 hrs.	10%	46.58%
B	7 "	10%	48.06
C	6 "	5%	44.77

Evidently, comparing B table 8, with G table 7,(from same sam-
ple) the agitation increases the speed of reaction.

Decomposition by Heating in Pressure Flasks.

It was thought that the regular reaction observed in the cold
might be effected more quickly by heating, if dissociation of the
NH_4Cl was prevented. Accordingly the experiment was tried with
closed saponification flasks. Under these conditions the pressure
of the liberated ammonia should force back and prevent any dissocia-
tion of NH_4Cl into NH_3 and HCl, which it had been thought might be
responsible for the variable results obtained when boiling in open
vessels. Oven-dry samples of 1.0 g. were used as before. The
NH_4Cl was dissolved in 100 c.c. of water. With samples B and D,
75 c.c. water and 25 c.c. strong ammonia was used instead, with the
idea of assuring the prevention of any dissociation of NH_4Cl, and

of observing the effect upon the speed of reaction. The flasks were immersed in a boiling water bath for 1 hour and 10 minutes, with occasional shaking. All of the CaO values given in these experiments are the mean of duplicates.

Table 9. Decomposition in Pressure Flasks.

Sample	NH_4Cl in 100 cc.	Ammonia	CaO
A	2. g.	none	41.71%
B	2. "	25 cc.	21.12
C	5. "	none	48.35
D	5. "	25 cc.	34.83

The effect of the ammonia in checking the speed of reaction is very striking. The speed naturally increases with the concentration of the NH_4Cl. The residue from sample C, which gives results nearest to those of the long period cold decompositions, was treated with hot dilute HCl for a few minutes and the insoluble silica obtained, weighed and corrected by HF. It gave 13.05% SiO_2. This should be compared with the totals of SiO_2 of decomposition given in table 6, which are from 2% to 3.7% higher, although the CaO yielded in these cases was somewhat less than in the sample above. This makes us suspect that the decomposition in the hot is not exactly the same as in the cold.

Another experiment, similar to the preceeding, was made varying the conditions. The flasks were kept in the bath for two hours and shaken occasionally. Air-dry cement was used and the results were figured back to the "oven-dry" basis, for comparison. Table 1. This obviates differences due to variations in drying different samples. One sample was run with NH_4NO_3, with the idea that this salt, which does not dissociate to give an acid, might produce more regular de-

composition than NH_4Cl. Used 100 c.c. of solution.

Table 10. Decomposition in Pressure Flasks (for 2 hours).

Sample	Solution (100 cc.)	CaO on "Air-dry."	CaO on "Oven-dry."
A	5% NH_4Cl	47.29%	47.42%
B	10% NH_4Cl	51.30	51.44
C	5% NH_4NO_3	45.67	45.79

The stronger NH_4Cl solution seems to produce greater decomposition than the average of the cold treatments. The NH_4NO_3 appears promising as a means for decomposition. It should be tried with other concentrations, periods of time, etc., and also in the cold.

Conclusions.

1. When treated with water in excess, the aluminates decompose quickly and the poly-basic silicates begin a slow process of breaking down to less basic compounds. (See table 2).

2. Boiling with NH_4Cl solution in open vessels decomposes the aluminates and some of the silicates completely, the proportion of the latter being quite variable.

3. Treated with cold NH_4Cl solutions, the amount of decomposition seems quite regular and well under control. It is not a rapid reaction, but the speed increases with the concentration and is accelerated by agitation. The ratio of the decomposition products favors the view that the aluminates and the tri-calcium silicate are completely decomposed, after a sufficient interval of time. The

undecomposed silicates are of two varieties, one of which dissolves completely in HCl while the other separates granular silica.

4. Decomposition with NH_4Cl in pressure flasks at the temperature of 100° gives results approaching those obtained in the cold, but there is evidence that the reactions take a somewhat different course from that in the latter case.

5. The separation of free silica from the reaction mixture is very unsatisfactory and makes the deductions somewhat uncertain.

The above conclusions are not given as final, but conditions have been shown under which cement is decomposed quite regularly, and this offers a basis for further investigations.

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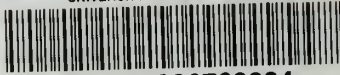   G. Goguelia.
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